

Description

[High Flow Engineering Thermoplastic Compositions and Products Made Therefrom]

BACKGROUND OF INVENTION

[0001] *FIELD OF THE INVENTION* The present invention relates to flow modified thermoplastic compositions for molding applications made from thermoplastic polymers and low molecular weight vinyl aromatic/(meth)acrylate polymeric modifiers.

[0002] Thermoplastics and thermoplastic blends for use in various engineering applications should exhibit a variety of favorable physical properties such as high heat resistance, high impact strength, high moldability and processability, and in some instances, good transparency. Polycarbonates, polyamides, polyesters and polyethers among other engineering thermoplastics are particularly popular components due to their toughness and relatively high softening temperatures. These favorable mechanical, and ther-

mal properties, as well as their good electrical properties make these resins widely applicable for engineering plastics in various fields, including the field of housings for electronic equipment and automobile parts. Due to their relatively poor melt flow characteristics, however, polycarbonates and other engineering plastics, are often blended with one or more additional polymers and additives to improve their melt flow properties. Generally, previous attempts to improve the melt flow characteristics of engineering thermoplastics have involved incorporating lower melting substances and/or less expensive polymers with lower melt viscosity into the thermoplastic. Unfortunately, the resulting blends generally exhibit improved melt flow characteristics at the expense of other valuable features, such as, impact strength and heat resistance. This trade-off is unacceptable, particularly when the thermoplastic materials are used as moldings for housings for electronics which require thin walls, as well as high impact strength and heat resistance.

[0003] Thus, a need exists for a thermoplastic composition that exhibits increased moldability and processability while retaining other desirable physical properties such as high heat resistance and impact strength.

SUMMARY OF INVENTION

[0004] The present invention makes use of low molecular weight, vinyl aromatic/(meth)acrylate polymers as flow enhancers for thermoplastics and thermoplastic blends to provide thermoplastic compositions with improved moldability and flowability for molding applications, while maintaining a good balance of impact and heat resistance. The thermoplastic compositions of the present invention are suitable for molding opaque and transparent housings for electronic devices, automobile parts, appliances, and other articles, particularly those exposed to high shear during molding. Typical applications are large molded parts or molded parts with thin walls, such as housings for mobile phones, laptop computers, personal computer CPU's and monitors, and other electronic devices, and housings for automobile control and indicator panels, mirrors, headlamps, etc. The compositions ensure excellent fluidity and moldability, and excellent surface appearance as well as high mechanical, thermal, and impact properties, without the incidence of delamination or additive juicing, and in some cases, without detriment to the transparency of the composition.

[0005] One aspect of the present invention provides a high flow

thermoplastic composition made from a host polymer and a flow modifier polymer having a low molecular weight, wherein the flow modifier polymer has a weight-average molecular weight of less than 15,000 and is made from at least one (meth)acrylate and optionally at least one vinyl aromatic monomer and the relative energy difference (R.E.D.) between the flow modifier and host polymer is less than 2.2 Preferred embodiments have an R.E.D. of less than 1.75. Additionally, in preferred embodiments the weight average molecular weight of the flow modifier is less than 10,000. Highly preferred embodiments include flow modifiers having a weight average molecular weight of 5,000.

[0006] Another aspect of the present invention provides a high flow thermoplastic composition made from a flow modifier polymer and a host polymer selected from the group consisting of polycarbonates, polycarbonate/acrylonitrile-butadiene-styrene blends, polyamides, polyesters, polyphenylene ethers, transparent-ABS resins, and combinations thereof. Highly preferred embodiments include polycarbonate host polymers or polycarbonate acrylonitrile-butadiene-styrene blend. Alternatively, the host polymer is selected from the group consisting of

polyamide, poly(butylene terephthalate), poly(propylene terephthalate), poly(ethylene terephthalate), PETG, polyethylene naphthalate, polyphenylene oxide, and combinations thereof.

- [0007] The host polymer is present in an amount of from about 50 to about 99 weight percent and the flow modifier polymer is present in an amount of from about 1 to about 20 weight percent.
- [0008] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer wherein the flow modifier polymer comprises (b1) 1–100 % of a (meth)acrylate monomer, (b2) 0–99% of at least one vinyl aromatic monomer, and (b3) 0–99% of another monomer or mix of monomers able to copolymerize with (b1) and (b2). Preferred embodiments include a flow modifier polymer comprising from about 1 to about 70 weight percent of at least one (meth)acrylate monomer and from about 30 to about 99 weight percent of at least one vinyl aromatic monomer.
- [0009] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer, wherein the said composi-

tion has a melt flow index at least 5 percent higher than the host polymer.

- [0010] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer, wherein the notched Izod impact strength of the said composition differs by no more than 40% from the notched Izod impact strength of the host polymer.
- [0011] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer, wherein the heat deflection temperature of the composition differs by no more than 10°C from the heat deflection temperature of the host polymer.
- [0012] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer, wherein the Vicat softening temperature of the composition differs by no more than 10°C from the Vicat softening temperature of the host polymer.
- [0013] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer, wherein the composition is a

transparent composition having a haze percentage that differs by less than about 1 % from the haze percentage of the host polymer.

- [0014] Still another aspect of the present invention provides a high flow polymer composition made from a flow modifier polymer and a host polymer, wherein the composition further comprises at least one additive wherein the additive is an impact modifier, a mineral filler, a pigment, a dye, or a fire retardant.
- [0015] A further aspect of the invention provides a flow thermoplastic composition wherein at least one vinyl aromatic monomer is styrene or a styrene derivative and the at least one (meth)acrylate monomer is selected from the group consisting of butyl methacrylate, methyl methacrylate, glycidyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, acrylic acid and maleic anhydride.
- [0016] One non-limiting example of a suitable composition according to the present invention contains (A) 50–99 % of an engineering thermoplastic chosen from the families of polycarbonates (PCs), polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) blends, polyesters and polyester based blends, polyamides and polyamide based blends, polyphenylene ether (PPE) based blends and

transparent ABS, (B) 1– 20 % of a low molecular weight polymer obtained by polymerizing (b1) 1–100 % of a (meth)acrylate monomer, (b2) 0 99% of at least one vinyl aromatic monomer, and (b3) 0–99% of other monomer or mix of monomers able to copolymerize with (b1) and (b2), (C) 0–20% of an impact modifier, (D) 0–50% of a mineral filler or reinforcing agent, (E) 0–10% of a suitable pigment or dye, and (F) 0–25% of a fire retardant or mix of fire retardant agents.

- [0017] Another aspect of the invention provides a method for increasing the flow of a host polymer by mixing therewith a flow modifier polymer having a weight average molecular weight (M_w) of less than about 15,000. Again, the flow modifier polymer is made from at least one (meth)acrylate monomer and optionally at least one vinyl aromatic monomer and the relative energy difference between the flow modifier and host polymer is less than 2.2.
- [0018] Still another aspect of this invention provides a molded article made from the high flow composition made from the host polymer and the flow modifier polymer.
- [0019] Another aspect of this invention provides a method for manufacture of a molded article wherein the article is an automobile part or a housing for a piece of electronic

equipment. The article may also be a housing for a computer, a computer monitor, a keyboard, a printer, a fax machine, a telephone, a mobile communications device, such as a mobile phone, a camera, a power plug, an electrical switch, an electrical connector, an electrical control panel, a telecommunication connector, a telecommunication switch, an automobile control panel, an automobile indicator panel, a mount for a mirror, an automobile headlamp, an automotive bumper, automotive fascia, an automotive hood, an engine cover, a generator cover, a battery cover, an air manifold, automotive hoses and connectors, a tractor hood, an automotive panel, a tractor panel, a lawn mower deck, a lawn tool, a piece of office equipment, including a photocopier, a tray for a photocopier, household electronics, such as coffee makers, irons, vacuum cleaners, and fans, large appliances, such as televisions, DVD players, refrigerators, washing machines, and dryers; or parts for a computer, a computer monitor, a keyboard, a printer, a fax machine, a telephone, a mobile communications device, such as a mobile phone, a camera, a power plug, an electrical switch, an electrical connector, an electrical control panel, a telecommunication connector, a telecommunication

switch, an automobile control panel, an automobile indicator panel, a mount for a mirror, an automobile head-lamp, an automotive bumper, automotive fascia, an automotive hood, an engine cover, a generator cover, a battery cover, an air manifold, automotive hoses and connectors, a tractor hood, an automotive panel, a tractor panel, a lawn mower deck, a lawn tool, a piece of office equipment, including a photocopier, a tray for a photocopier, household electronics, such as coffee makers, irons, vacuum cleaners, and fans, large appliances, such as televisions, DVD players, refrigerators, washing machines, and dryers.

- [0020] Another aspect of this invention provides high flow thermoplastic compositions comprising of a host polymer and low molecular weight flow modifier polymer wherein the flow modifier polymer is substantially free of acrylonitrile.
- [0021] Another aspect of this invention provides a method for increasing the flow of a host polymer comprising mixing the host polymer with a flow modifier polymer having a weight average molecular weight of less than about 15,000, the flow modifier polymer comprising at least one vinyl aromatic monomer and at least one (meth)acrylate monomer wherein the said composition is characterized

by a relative energy difference (R.E.D.) between the flow modifier polymer and the host polymer of less than 2.2.

[0022] Another aspect of the invention provides a method for manufacturing high flow engineering thermoplastic compositions by mixing a host polymer and a low molecular weight flow modifier polymer, the flow modifier polymer comprising at least one (meth)acrylate monomer and optionally at least one vinyl aromatic monomer, to form a flow modified thermoplastic composition; and molding the flow modified thermoplastic composition, wherein the mixing and molding steps have a maximum processing temperature, and further wherein the flow modifier polymer undergoes a weight loss of less than about 10 % at the maximum processing temperature. In various embodiments of this method, the weight average molecular weight of the flow modifier polymer is less than about 15,000 and the maximum processing temperature is at least 180°C.

[0023] Another aspect of this invention provides a method for processing a high flow thermoplastic composition comprising mixing a host polymer and a flow modifier polymer having a weight average molecular weight of less than about 15,000, the flow modifier polymer comprising

at least one vinyl aromatic monomer and at least one (meth)acrylate monomer to form a flow modified thermoplastic composition wherein the said composition is characterized by a relative energy difference (R.E.D.) between the flow modifier polymer and the host polymer of less than 2.2; and molding the flow modified thermoplastic composition, wherein the mixing and molding steps have a maximum processing temperature of up to about 350 °C, and further wherein the flow modifier polymer undergoes a weight loss of less than about 10 % at the maximum processing temperature. It is preferred that the maximum processing temperature be above 180 °C.

[0024] Another aspect of this invention provides a method for processing a high flow thermoplastic composition wherein the mixing and molding steps are carried out at shear rates in excess of $100,000 \text{ sec}^{-1}$. Alternative methods can be carried out at shear rates in excess of $300,000 \text{ sec}^{-1}$ or $500,000 \text{ sec}^{-1}$.

DETAILED DESCRIPTION

[0025] A first aspect of the invention provides a high flow thermoplastic composition made from a host polymer blended with a low molecular weight vinyl aromatic/(meth)acrylate flow modifier polymer.

[0026] The invention is based on the inventors" discovery that low M_w vinyl aromatic/(meth)acrylate resins may be used as flow enhancers in engineering thermoplastic compositions, providing such compositions with improved moldability (a.k.a. flowability) for injection molding applications, particularly those exposed to very high shear rates. Very high shear rates greater than $10,000\text{s}^{-1}$ are included. Very high shear rates also include shear rates greater than $50,000\text{s}^{-1}$, shear rates greater than $100,000\text{s}^{-1}$, shear rates greater than $200,000\text{s}^{-1}$, shear rates greater than $300,000\text{s}^{-1}$, shear rates greater than $400,000\text{s}^{-1}$, shear rates greater than $500,000\text{s}^{-1}$, and shear rates greater than $1,000,000\text{s}^{-1}$. Molded products made from the modified thermoplastics maintain a good balance of impact, mechanical, and heat resistance properties without delamination, additive juicing or blooming problems or detriment to the transparency when applicable.

[0027] The thermoplastic compositions are useful for housings for electronics and automobile parts which require thinner and thinner walls without losing a satisfactory balance of mechanical, impact and thermal properties, and transparency when required. Additionally, molding thin walled or large intricate parts requires minimization of the vis-

cosity, and thus the shear rates in the mold, by employing extreme temperature conditions. The flow modifiers of this invention provide formulations with much lower melt viscosity at given temperatures than other presently available flow modifiers. This provides decreased shear rates and stresses during the molding process and/or allows for lower temperature molding, thus offering energy cost savings.

[0028] Without wishing or intending to be bound to any particular theory of the invention, the inventors believe the superior performance of the flow modifiers (FMs) may be explained by their very high compatibility and/or miscibility with the host polymers. Compatibility and/or miscibility are controlled in this invention by optimizing the intermolecular interactions between the flow modifiers and the host polymers. These interactions include but are not limited to Van der Waals forces, including London Dispersion forces and dipole-dipole interactions, and/or hydrogen bonding. A flow modifier having a combination of suitably high intermolecular interactions with a given host polymer and a suitably low molecular weight appears to provide the key to optimizing the compatibility. This high compatibility with the host polymer is believed to allow the flow

modifiers to maximize the flow and minimize the melt viscosity of the composition while minimizing adverse effects on thermal, mechanical, and impact properties. It is likely also that this high compatibility prevents delamination, blooming, juicing and other phase separation effects common in the art of high temperature and high shear rate molding. The high compatibility is further believed to be responsible for the high transparency observed in the transparent compositions of this invention even when sizeable refractive index (R.I.) mismatches exist between the transparent host polymer and the flow modifiers.

[0029] The flow modifier polymers are low molecular weight polymers made by polymerizing at least one (meth)acrylate monomer and optionally at least one vinyl aromatic monomer. A low molecular weight flow modifier polymer may be any flow modifier polymer having a sufficiently low molecular weight to act as a flow enhancer, in some instances without having a substantial negative effect on the mechanical properties, such as impact strength and heat resistance, of the resulting thermoplastic composition. In various embodiments of the invention, the flow modifiers are polymers having a M_w , as measured using gel permeation chromatography, of less than

15,000. Thus, low molecular weight flow modifier polymers also include polymers having a M_w of less than 10,000, polymers having a M_w of less than 9,000, polymers having a M_w of less than 8,000, polymers having a M_w of less than 7,000, polymers having a M_w of less than 6,000, polymers having a M_w of less than 5,000, polymers having a M_w of less than 4,000, polymers having a M_w of less than 3,000, polymers having a M_w of less than 2,000, polymers having a M_w of less than 1,000, and polymers having a M_w of less than 500.

[0030] In addition to possessing low molecular weights, due to their monomer compositions these flow modifiers are also substantially compatible with the host polymers. One method of determining the compatibility of a given blend is by calculating the solubility parameter differences between the flow modifiers and host plastics as described in the Polymer Handbook, 4th Ed., pp. 675 688 and Hansen Solubility Parameters A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 13, which is incorporated herein by reference. The solubility parameter difference is defined as:

[0031]

$$R_{ij} = [4(\delta_{Di} - \delta_{Dj})^2 + (\delta_{Pi} - \delta_{Pj})^2 + (\delta_{Hi} - \delta_{Hj})^2]^{0.5}$$

[0032] where i refers to the flow modifier, j refers to the host plastic, δ_D refers to dispersion solubility parameter, δ_P to the polar solubility parameter, and δ_H to the hydrogen bonding solubility parameter.

[0033] In general, the mechanical properties of the thermoplastic compositions are maximized and the adverse affects of delamination, blooming, juicing and other phase-separation type problems are minimized by decreasing the solubility parameter differences between host polymer and flow modifier. A very good measure of compatibility is determined by the Relative Energy Difference (R.E.D. number) between the flow modifiers and the host plastics as defined in Hansen Solubility Parameters A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 – 13. The R.E.D. number is defined as:

$$[0034] R.E.D. = R_{ij}/R_o$$

[0035] where R_o is the radius of interaction for the host plastic as defined in Hansen Solubility Parameters – A Users Handbook, C.M. Hansen, CRC Press 2000, pp.1-13. In general, the mechanical properties of the thermoplastic compositions are maximized with the adverse affects of delamination, blooming, juicing and other phase-separation type problems are minimized by decreasing the R.E.D. number. Thus, in various embodiments, the compositions may have a R.E.D. number of less than 2.2. Preferably, the R.E.D. number is less than 1.75. This includes embodiments where the R.E.D. number is less than about 1.0,

less than about 0.8, less than about 0.6, or even less than about 0.5.

[0036] The improved flow characteristics of the modified thermoplastic compositions may be shown by the increase in the melt flow index (MFI) of the modified host polymer (i.e. the host polymer plus the flow modifier polymer) as compared to the melt flow index of the unmodified host polymer. The MFI provides a measure of the rate of extrusion of a thermoplastic through an orifice at a prescribed temperature and load. The ASTM D-1238 test for MFI provides a common and standardized test for measuring the MFI for a given specimen. Although the amount of the flow modifier added to the host polymers will vary widely depending on such factors as the nature of the host plastic and the flow modifier, and the intended application of the final product, in various embodiments of the invention, the flow modifiers will be present in an amount sufficient to increase the MFI, as measured by ASTM D-1238, of the modified thermoplastic (i.e. the host polymer plus the flow modifier polymer) as compared to the unmodified thermoplastic by at least 5 %. This includes embodiments where the MFI, as measured by ASTM D-1238, is increased by at least 10 %, at least 20 %, at least 30 %, at

least 40 %, and at least 50 %. In various embodiments, the high flow thermoplastic compositions will contain from about 1 to about 20 weight percent of the flow modifier polymer. This includes compositions that contain from about 1 to about 10 weigh percent of the flow modifier polymer, and compositions that contain from about 1 to about 5 weigh percent of the flow modifier polymer.

[0037] An advantage of the flow modifiers of this invention is that they provide improved flowability, and therefore processability, without sacrificing impact strength or heat resistance. This may be demonstrated by the high impact strengths of the modified thermoplastic compositions and the products made therefrom. The impact strength of a material is simply a measure of the amount of energy required to break a specimen of the material. The ASTM D-256 test for impact strength provides a common and standardized test for measuring the impact strength of a notched specimen (i.e. the "notched impact strength"). The notched impact strength of the modified thermoplastics of this invention may vary depending on a variety of factors, including the nature of the host plastic and the flow modifier, as well as the intended application for the modified thermoplastic itself and processing conditions.

However, in some embodiments of the invention, the modified host polymers and the compositions made therefrom demonstrate a notched impact strength which is changed when compared to the unmodified host plastic by as little as -40%. This includes embodiments where the impact resistance, measured according to ASTM D-256 is changed by -30%, -20%, -10%, and 0%. In some embodiments of the invention, the modified host polymers and the compositions made therefrom demonstrate a notched impact strength which is changed when compared to the unmodified host plastic by +40%. This includes embodiments where the impact resistance, measured according to ASTM D-256 is changed by +30%, +20%, +10% and 0%.

[0038] The heat resistance of the modified thermoplastic compositions may be measured by the heat deflection temperature (HDT) or by the Vicat Softening temperature (VST) of the compositions. The HDT or VST provides a measure of the temperature at which an arbitrary deformation occurs when a specimen of the material of interest is subjected to a flexural load. The ASTM D-648 test for HDT and VST provides a common and standardized test for measuring the HDT of a specimen. Like the notched impact strength, the HDT or VST of the modified thermoplastics of this in-

vention may vary depending on a variety of factors, including the nature of the host plastic and the flow modifier, as well as the intended application for the modified thermoplastic itself and processing conditions. However, in some embodiments of the invention, the modified host polymer and compositions made therefrom demonstrate an HDT or VST, measured according to ASTM D-648 which is changed when compared to the unmodified host plastic by as little as -10°C. This includes embodiments where the HDT, measured according to ASTM D-648 is changed by -7°C, -5°C, -2°C, and 0°C. In some embodiments of the invention, the modified host polymers demonstrate an HDT or VST, measured according to ASTM D-648 which is changed when compared to the unmodified host plastic by up to +10°C. This includes embodiments where the HDT, measured according to ASTM D-648 is changed by +7°C, +5°C, +2°C, and 0°C.

[0039] In certain applications it is desirable to provide transparent thermoplastic compositions. Unlike many of the flow enhancers currently available, the flow enhancers of the present invention do not significantly degrade the transparency of transparent thermoplastic host polymers, such as polycarbonates, transparent polyesters, and transpar-

ent ABS resins. Thus, high flow transparent thermoplastics may be achieved when starting with transparent engineering thermoplastics and adding the low molecular weight flow agents. The transparency of the flow modified thermoplastics may be measured by the haze of the material. Haze is a measure of the scattering of light as it passes through a transparent material. The ASTM D-1003 test for haze provides a common and standardized test for measuring the haze of a specimen. Using the flow modifiers of the present invention in combination with transparent host polymers may provide high flow, transparent thermoplastic compositions having a haze, as measured by ASTM D-1003 which is changed when compared to the haze of the unmodified host plastic by as little as +1.0%. This includes embodiments where the haze, measured according to ASTM D-1003 is changed by +0.7%, +0.5%, +0.2% and 0%. This also includes embodiments where the haze, measured according to ASTM D-1003 is changed by -1.0%, -0.7%, -0.5%, -0.2% and 0%.

[0040] The host polymer may be any engineering thermoplastic or blend of thermoplastics for use in molding applications. Examples of suitable host polymers include, but are not limited to, polycarbonates, polyamides, polyesters,

polyphenylene ethers, and transparent ABS resins. Due to their favorable mechanical properties, polycarbonates or blends of polycarbonates with elastomeric graft polymer resins, such as acrylonitrile–butadiene–styrene (ABS) resins, are particularly suitable host polymers.

[0041] Polycarbonate host polymers included in the compositions may be any aliphatic or aromatic homopolycarbonate or copolycarbonate known in the art. These polycarbonates may be manufactured according to conventional processes. Thermoplastic aromatic polycarbonates suitable for use in the compositions of the present invention include polycarbonates generally prepared by the reaction of dihydric phenols with a carbonate precursor, such as phosgene or carbonate compounds. Examples of suitable dihydric phenols include, but are not limited to, dihydroxy diphenyls, bis-(hydroxy phenyl)-alkanes, bis-(hydroxy phenyl)-cycloalkanes, bis-(hydroxy phenyl)-sulphides, bis-(hydroxy phenyl)-ethers, bis-(hydroxy phenyl)-ketones, bis-(hydroxy phenyl)-sulfoxides, bis-(hydroxy phenyl)-sulphones, α,α -bis-(hydroxy phenyl)-diisopropyl benzenes, and combinations thereof.

[0042] Specific examples of suitable dihydric phenols include, but are not limited to, 2,2-bis (4-hydroxyphenyl)propane

(bisphenol A), bis (hydroxyaryl) alkanes such as bis (4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)octane, 2,2-bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxy-1-methylphenyl)propane, bis(4-hydroxyphenyl)naphthylmethane, 1,1-bis(4-hydroxy-t-butylphenyl)propane, 2,2-bis(4-hydroxy-3,5-tetramethylphenyl)propane; bis(hydroxyaryl)cycloalkanes such as 1,1-bis (4-hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)-3,5,5-trimethylcyclohexane; dihydroxyaryl ethers such as 4,4'-dihydroxyphenyl ether, 4,4'-dihydroxy-3,3'-dimethylphenyl ether; dihydroxydi-aryl sulfides such as 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfide; dihydroxy-diaryl sulfoxides such as 4,4'-dihydroxydiphenyl sulfoxide, 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfoxide; dihydroxydiaryl sulfones such as 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfone; dihydroxydiphenyls such as 4,4'-dihydroxydiphenyl.

[0043] ABS resins for use in PC/ABS or transparent-ABS host polymers are well-known in the art. The ABS resins suitable for use in the host polymers are generally formed from a rigid graft polymer grafted to a diene rubber. Typically, the ABS resins have a continuous phase made from styrene and acrylonitrile monomers on a discontinuous elastomer phase based on a butadiene elastomer. In these resins the two phases are generally linked by grafting the styrene/acrylonitrile copolymer onto the polybutadiene. However, the scope of the ABS resins suitable for use in the present invention also encompasses elastomeric resins formed from a monovinylidene aromatic monomer other than styrene and from acrylate or methacrylate monomers rather than or in addition to the acrylonitrile monomer. In addition, the diene rubbers are not limited to butadiene rubbers. The relative proportions of the PC and the ABS in the PC/ABS host polymer blends may vary over a wide range and will depend in part on the intended application of the composition. In one exemplary embodiment, the PC/ABS host polymer blends contain from about 95 to about 50 weight percent PC and from about 5 to about 50 weight percent ABS.

[0044] When the flow modified thermoplastic is to be used in a

transparent application, transparent-ABS is a particularly suitable host polymer. Conventional transparent ABS resins are rubber-reinforced resins produced by graft-polymerizing methyl methacrylate (MMA), styrene (ST) and acrylonitrile (AN) in the presence of polybutadiene. The MMA/ST/AN terpolymer obtained by the graft polymerization exhibits a refractive index close to that of polybutadiene.

[0045] Polyamides are another example of a suitable host polymer for use in the present compositions. Polyamides (PAs) are well known and commercially available. These thermoplastic polymers cover a range of polymers containing recurring amide groups in the main polymer chain. Mixtures of various polyamides, as well as various polyamide copolymers, are also useful as host polymers. The polyamides can be obtained by a number of well known processes such as those described in U.S. Patent Nos. 2,071,250; 2,071,251; 2,130,523; 2,130,948; 2,241,322; 2,312,966; and 2,512,606, which are incorporated herein by reference. Nylon-6, for example, is a polymerization product of caprolactam. Nylon-6,6 is a condensation product of adipic acid and 1,6-diaminohexane. Likewise, nylon 4,6 is a condensation product between adipic acid

and 1,4-diaminobutane. Besides adipic acid, other useful diacids for the preparation of nylons include azelaic acid, sebacic acid, dodecane diacid, as well as terephthalic and isophthalic acids, and the like. Other useful diamines include m-xylylene diamine, di-(4-aminophenyl)methane, di-(4-aminocyclohexyl)methane; 2,2-di-(4-aminophenyl)propane, 2,2-di-(4-aminocyclohexyl)propane, among others.

Copolymers of caprolactam with diacids and diamines are also useful. Examples of polyamides suitable for use in the present invention include, but are not limited to, those polyamides known as PA 6, PA 6,6; PA 6,12; PA 11; PA 12; and PA 6,9.

[0046] Polyesters may also be used as the host polymer in the compositions. Polyesters are well known in the art and include a variety of polymers produced through the polycondensation of hydroxycarboxylic acids or dicarboxylic acids with dihydroxy compounds. Polyesters suitable for use in the present invention are thermoplastic polyesters and include all heterochain macromolecular compounds that possess repeat carboxylate ester groups in the backbone of the polymer. Mixtures of various polyesters, as well as various polyester copolymers, are also useful as

host polymers. Examples of suitable polyesters include, but are not limited to, poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET), PETG, poly(ethylene-co-cyclohexyldimethanol terephthalate), amorphous polyesters, polyethylene naphthalate (PEN), and poly(propylene terephthalate) (PPT).

[0047] Polyphenylene ethers are also suitable for use as the host polymers in the compositions of the present invention. The term polyphenylene ether resin includes unsubstituted polyphenylene ether polymers, substituted polyphenylene ether polymers wherein the aromatic ring is substituted, and blends thereof. Mixtures of various polyphenylene ethers, as well as various polyphenylene copolymers, are also useful as host polymers. Polyphenylene oxide (PPO) is one non-limiting example of a polyphenylene ether.

[0048] Blends of two or more of the thermoplastic polymers listed above or blends of the thermoplastic polymers listed above with other polymers may also be used as host polymers. Examples of suitable blends include polycarbonate/polyester blends, such as PC/PBT, PC/PET blends, blends of polyacrylates with polystyrenes, blends including polyolefins or ABS resins such as polyamide/ABS and

polyamide/polyolefines, such as polyethylene, or polypropylene, and blends of polyphenylene ethers with polystyrenes (including high impact polystyrene), or polyamides. When the host polymer is itself a blend of two or more polymers, the weight percentages quoted throughout this specification refer to total weight percentages for the multipolymer blends.

[0049] The flow modifiers of the present invention are low molecular weight polymers and copolymers made by polymerizing at least one (meth)acrylate monomer and optionally at least one vinyl aromatic monomer. As used herein, the term (meth)acrylate is intended to indicate both acrylate and methacrylate monomers. It should be noted that while some host polymers, particularly those that include a graft polymer resin, such as ABS, may themselves include both vinyl aromatic and (meth)acrylate monomers, the low molecular weight flow modifiers are distinct components of the compositions of this invention. In particular, the flow modifiers are not diene-based graft polymers or other rubber based polymers.

[0050] In some embodiments of the invention the flow modifier polymer contains only (meth)acrylate monomers. In other embodiments the flow modifier polymer contains from

about 1 to about 99 weight percent (meth)acrylate monomer and from about 99 to about 1 weight percent vinyl aromatic monomer. This includes embodiments containing from about 1 and about 70 weight percent of (meth)acrylate monomers and from about 30 to about 99 weight percent vinyl aromatic monomers, and further includes embodiments containing from about 1 to about 80 weight percent (meth)acrylate monomers and from about 20 to about 99 weight percent vinyl aromatic monomers. In some embodiments the flow modifier polymer also contains from about 0 to about 99 weight percent of at least one other monomer or a mixture of other monomers capable of polymerizing with the (meth)acrylate monomers and/or the vinyl aromatic monomers. This includes embodiments that contain about 1 to about 70 weight percent of at least one other monomer or a mixture of other monomers capable of polymerizing with the (meth)acrylate monomers and/or the vinyl aromatic monomers.

[0051] Exemplary (meth)acrylate monomers include both functional and non-functional monomers. Suitable acrylate and methacrylate monomers include, but are not limited to, methyl acrylate, ethyl acrylate, n-propyl acrylate, i-

propyl acrylate, n-butyl acrylate, s-butyl acrylate, i-butyl acrylate, t-butyl acrylate, n-amyl acrylate, i-amyl acrylate, isobornyl acrylate, n-hexyl acrylate, 2-ethylbutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate, methylcyclohexyl acrylate, cyclopentyl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, i-propyl methacrylate, i-butyl methacrylate, n-amyl methacrylate, n-hexyl methacrylate, i-amyl methacrylate, s-butyl-methacrylate, t-butyl methacrylate, 2-ethylbutyl methacrylate, methylcyclohexyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, and isobornyl methacrylate. Examples of epoxy-functional (meth)acrylate monomers for use in the present invention, include both acrylates and methacrylates. Examples of these monomers include, but are not limited to, those containing 1,2-epoxy groups such as glycidyl acrylate and glycidyl methacrylate. The epoxy-functional monomer glycidyl methacrylate is a particularly suitable monomer. Examples of acid functional monomers include, but are not limited to, acrylic acid and methacrylic acid. Examples of hydroxy functional monomers include, but

are not limited to, hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA). Examples of amine functional monomers include, but are not limited to, dimethylaminoethyl methacrylate (DMAEMA) and dimethylaminoethyl acrylate (DMAEA).

- [0052] Vinyl aromatic monomers include both styrene and styrene derivatives, such as styrene, α -p-methylstyrene, 3,4-dimethylstyrene, o- and p-divinyl benzene, α -chlorostyrene, 2,4-dichlorostyrene and p-chloro- α -methylstyrene, o, m or p-bromostyrene, and di-bromostyrene. Vinyl toluene is an additional example of a suitable aromatic monomer for use in the flow modifiers.
- [0053] In addition to the vinyl aromatic monomers and the (meth)acrylate monomers, the modifier polymer may include other monomers which are able to copolymerize with the aromatic vinyl monomers and the methacrylate monomers. Such additional monomers include, but are not limited to, maleic anhydride, maleic acid and its mono and diesters, fumaric acid and its mono and diesters, vinyl acetate and the esters of vinyl alcohol, α -olefines and diene monomers, vinyl chloride, acrylonitrile.
- [0054] In various embodiments of the invention, the modifier polymer does not include nitrile or acrylonitrile

monomers. This is advantageous because many nitrile and acrylonitrile monomers are toxic.

- [0055] In addition to the host polymer and the modifier polymer, the high-flow thermoplastic compositions may optionally include other additives such as impact modifiers, inorganic or mineral fillers, reinforcing agents, pigments, dyes, and fire retardants.
- [0056] Impact modifiers for thermoplastic compositions are well known in the art and are commercially available. Examples of impact modifiers include thermoplastic elastomer based modifiers, including acrylic impact modifiers, such as methyl methacrylate–butadiene–styrene (MBS) impact modifiers, styrene–butadiene (SB) impact modifiers, styrene–butadiene–styrene (SBS) impact modifiers, and styrene–isoprene–styrene (SIS) impact modifiers.
- [0057] Inorganic and mineral fillers and reinforcing agents for use in the thermoplastic compositions are well known in the art. These are typically added to thermoplastic resins, such as polycarbonate resins, for the purpose of improving the mechanical strength and/or the durability of the thermoplastic composition. Examples include, but are not limited to, glass fibers, carbon fibers, glass beads, carbon black, calcium sulfate, calcium carbonate, calcium silicate,

titanium oxide, alumina silica asbestos, talc, clay mica and quartz powder. In addition, a mixture of any of the above may be used.

[0058] A variety of flame retardants for use with thermoplastic compositions are also well known. Perhaps the most popular of these are phosphate and phosphonate based flame retardants. Examples of well-known flame retardants from the prior art include organic phosphate esters such as triphenyl phosphate, tricresyl phosphate, diphenylcresyl phosphate, resorcinol diphenyl phosphate and various other oligomeric phosphates. Tetrafluoroethylene polymers are also used in combination with such phosphate esters in order to provide flame retardancy. Many of these phosphorous based flame retardants incidentally act as flow enhancers. Unfortunately, while these phosphate based flame retardants can improve flame retardancy and flow, at high loadings these flame retardants also tend to have a negative effect on the impact strength and heat resistance of the thermoplastic compositions. Thus, one advantage offered by the compositions of the present invention over the compositions of the prior art is that by the using flow modifiers disclosed herein, the amount of phosphate flame retardant may be reduced without sacri-

ficing flame retardancy, impact strength, or heat resistance.

[0059] Another advantage of the flow modifiers of the present invention is that they are flame neutral, that is, they neither improve nor decrease the flame retardancy of the compositions. Another advantage of the flow modifiers of the present invention is that they do not increase dripping under UL-94 testing even in the highest flow compositions. Thus, the flow modifiers may be used in either flame retardant or non-flame retardant compositions.

[0060] The flow modified thermoplastics of the present invention are well suited for a variety of applications. Examples of products that may be manufactured from the thermoplastics include, but are not limited to, housings for electronic equipment, business machines, such as computers, monitors, keyboards, printers, fax machines, telephones, notebook and handheld computers, and cameras, power plugs, electrical switches and controls, and telecommunication connectors and switches. In addition, the compositions may be used to make a variety of parts in the automotive industry, including, control and indicator panels, mirrors, headlamps, automotive bumpers and fascia, tractor hoods and panels, lawn mower decks, lawn and gar-

den tool housings, and various other large structural parts.

- [0061] Another aspect of the invention provides a method for increasing the flow of a host polymer by mixing therewith a flow modifier polymer. Again, the modifier polymer is made from at least one (meth)acrylate monomer and optionally at least one vinyl aromatic monomer. Suitable host polymers and flow modifier polymers are described in detail above.
- [0062] The low molecular weight flow modifier polymers may be produced according to standard techniques well known in the art. Such techniques include, but are not limited to, continuous bulk polymerization processes, batch, and semi-batch polymerization processes. A production technique that is well suited for the low molecular weight flow modifier polymers is described in *OLE_LINK1 US Patent 6,605,681 OLE_LINK1*, the entire disclosure of which is incorporated herein by reference. Briefly, this process involves continuously charging into a reactor at least one (meth)acrylate monomer, optionally at least one vinyl aromatic monomer, and optionally one or more other monomers that are polymerizable with the vinyl aromatic and (meth)acrylate monomers. The proportion of

monomers charged into the reactor may be the same as those proportions that go into the flow modifier polymers discussed above. Thus, the reactor may be charged with only (meth)acrylate monomers. Alternatively, the reactor may be charged with from about 1 to about 99 weight percent (meth)acrylate monomer and from about 99 to about 1 weight percent vinyl aromatic monomer. This includes embodiments where the reactor is charged with from about 1 and about 70 weight percent of (meth)acrylate monomers and from about 30 to about 99 weight percent vinyl aromatic monomers, and further includes embodiments where the reactor is charged with from about 1 to about 80 weight percent (meth)acrylate monomers and from about 20 to about 99 weight percent vinyl aromatic monomers. In some embodiments the reactor is also charged with from about 0 to about 99 weight percent of at least one other monomer or a mixture of other monomers capable of polymerizing with the (meth)acrylate monomers and/or the vinyl aromatic monomers. This includes embodiments where the reactor is charged with about 1 to about 70 weight percent of at least one other monomer or a mixture of other monomers capable of polymerizing with the (meth)acrylate

monomers and/or the vinyl aromatic monomers.

[0063] The reactor may also optionally be charged with at least one free radical polymerization initiator and/or one or more solvents. Examples of suitable initiators and solvents are provided in *US Patent 6,605,681*. Briefly, the initiators suitable for carrying out the process according to the present invention are compounds which decompose thermally into radicals in a first order reaction, although this is not a critical factor. Suitable initiators include those with half-life periods in the radical decomposition process of about 1 hour at temperatures greater or equal to 90°C and further include those with half-life periods in the radical decomposition process of about 10 hours at temperatures greater or equal to 100°C. Others with about 10 hour half-lives at temperatures significantly lower than 100°C may also be used. Suitable initiators are, for example, aliphatic azo compounds such as

1-t-amylazo-1-cyanocyclohexane, azo-bis-isobutyronitrile and 1-t-butylazo-cyanocyclohexane, 2,2"-azo-bis-(2-methyl)butyronitrile and peroxides and hydroperoxides, such as t-butylperoctoate, t-butyl perbenzoate, dicumyl peroxide, di-t-butyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, di-t-amyl perox-

ide and the like. Additionally, di-peroxide initiators may be used alone or in combination with other initiators. Such di-peroxide initiators include, but are not limited to, 1,4-bis-(t-butyl peroxy-carbo)cyclohexane, 1,2-di(t-butyl peroxy)cyclohexane, and 2,5-di(t-butyl peroxy)hexyne-3, and other similar initiators well known in the art. The initiators are di-t-butyl peroxide and di-t-amyl peroxide are particularly suited for use in the invention.

- [0064] The initiator may be added with the monomers. The initiators may be added in any appropriate amount, but preferably the total initiators are added in an amount of about 0.0005 to about 0.06 moles initiator(s) per mole of monomers in the feed. For this purpose initiator is either admixed with the monomer feed or added to the process as a separate feed.
- [0065] The solvent may be fed into the reactor together with the monomers, or in a separate feed. The solvent may be any solvent well known in the art, including those that do not react with the epoxy functionality on the epoxy-functional acrylic monomer(s) at the high temperatures of the continuous process described herein. The proper selection of solvent may decrease the gel particle formation during the continuous, high temperature reaction of the present in-

vention. Such solvents include, but are not limited to, xylene, toluene, ethyl-benzene, Aromatic-100™, Aromatic-150™, Aromatic- 200™ (all Aromatics available from Exxon), acetone, methylethyl ketone, methyl amyl ketone, methyl-isobutyl ketone, n-methyl pyrrolidinone, and combinations thereof. When used, the solvents are present in any amount desired, taking into account reactor conditions and monomer feed. In one embodiment, one or more solvents are present in an amount of up to 40% by weight, up to 15% by weight in a certain embodiment, based on the total weight of the monomers.

- [0066] The reactor is maintained at an effective temperature for an effective period of time to cause polymerization of the monomers to produce a polymeric product from the monomers.
- [0067] The continuous process of the present invention allows for a short residence time within the reactor. The residence time is generally less than one hour, and may be less than 15 minutes. In another embodiment, the residence time is generally less than 30 minutes, and may be less than 20 minutes.
- [0068] The process of the present invention may be conducted using any type of reactor well-known in the art, in a con-

tinuous configuration. Such reactors include, but are not limited to, continuous stirred tank reactors ("CSTRs"), tube reactors, loop reactors, extruder reactors, or any reactor suitable for continuous operation.

[0069] A form of CSTR which has been found suitable for carrying out the process is a tank reactor provided with cooling coils and/or cooling jackets sufficient to remove any heat of polymerization not taken up by raising the temperature of the continuously charged monomer composition so as to maintain a preselected temperature for polymerization therein. Such a CSTR may be provided with at least one, and usually more, agitators to provide a well-mixed reaction zone. Such CSTR may be operated at varying filling levels from 20 to 100% full (liquid full reactor LFR). In one embodiment the reactor is more than 50% full but less than 100% full. In another embodiment the reactor is 100% liquid full.

[0070] The low molecular weight flow modifier polymers of the present invention possess high thermal stability. Therefore, it is possible to process these polymers at higher temperatures than other flow modifiers. The high thermal stability of the flow modifiers of this invention is related to the fact that the process of the present invention is it-

self conducted in a continuous process at high temperatures. In one embodiment, the temperatures range from about 180°C to about 350°C, this included embodiments where the temperatures range from about 190°C to about 325°C, and more further included embodiment where the temperatures range from about 200°C to about 300°C. In another embodiment, the temperature may range from about 200°C to about 275°C. Due to their high temperature synthesis the flow modifiers of this invention show high thermal stability when used later in compounding and molding applications in engineering thermoplastic compositions processed at similar temperature ranges. In contrast other flow modifiers presently available undergo degradation and gas evolution at these conditions.

- [0071] One measure of the thermal stability of the flow modifier polymers is provided by thermogravimetric analysis (TGA). TGA monitors the weight loss of a polymeric specimen as a function of temperature. In various embodiments, the flow modifiers of the present invention are characterized by less than a 10 percent weight loss at the highest processing temperatures utilized in the processing of the modified thermoplastic compositions. This includes embodiments where the weight loss of the flow modifier is

less than 5 percent and further includes embodiments where the weight loss of the flow modifier is less than 3 percent at the highest processing temperature for the modified thermoplastic compositions. In some embodiments, the weight loss of the flow modifier is less than 1 percent at the highest processing temperature for the modified thermoplastic compositions. In some embodiments, zero weight loss of the flow modifier is measured at the highest processing temperature for the modified thermoplastic compositions.

[0072] The host polymers, the flow modifiers, and any optional ingredients can be blended according to any conventional techniques. For example, the components may be blended in a mixing and compounding apparatus, including, but not limited to, a single or twin screw extruder, mixing roll, ribbon blender or co-kneader. The thermoplastic compositions may be molded by various well-known molding techniques, such as injection molding, blow molding, compression molding, and extrusion molding. In some instances, the highest processing temperature realized during processing of the flow modified thermoplastic compositions will be at least 180°C, and, in some cases, will be from about 180 to about 350°C. This includes instances

where the highest processing temperature realized is at least 190°C, and in some cases is from about 190 to about 325°C. In other embodiments the maximum processing temperature is at least 200°C, and may be from about 200 to about 300°C, or even from about 200 to about 275°C.

[0073] The invention will be further described with reference to the following non-limiting examples.

[0074] *EXAMPLES*

[0075] Unless otherwise indicated, in what follows, all the exemplified compounding was carried out in a Leistritz 40-mm twin screw co-rotating extruder operating at 250 RPM. Injection Molding of ASTM test specimens was carried out in a Boy 50 injection molding machine with a clamping force of 50 metric tons, fitted with a 28-mm injection screw and a Procan II process monitoring system. Previous to compounding, and then previous to injection molding all thermoplastics and compounds, respectively, were dried according to thermoplastic manufacturer recommendations. Moisture levels were maintained below 0.05% (w/w) before molding.

[0076] *I. High Flow Polycarbonate Compositions*

[0077] *Preparation of Flow Modifiers I:*

[0078] In order to provide high flow in polycarbonate formulations for injection molding applications, four different styrene-acrylic flow modifiers, labeled FM A-D below, were designed and prepared in a 2 gallon free radical continuous polymerization reactor system according to the teachings of *US Patent 6,605,681*, the entire disclosure of which is incorporated herein by reference. The specific synthesis conditions and characterization parameters are given in Table 1 below. The abbreviations used below are defined as follows, STY = styrene, BMA = butyl methacrylate, MMA = methyl methacrylate, GMA = glycidyl methacrylate, BA = butyl acrylate, DTBP = di-tertiary butyl peroxide, A-100 = Aromatic 100 solvent (Exxon).

Table 1. Flow Modifier Preparation I.

	Flow Modifier A	Flow Modifier B	Flow Modifier C	Flow Modifier D
Monomer Feed Composition (% of monomer feed)				
STY	100	80	94.4	20
BMA	---	---	---	---
MMA	---	20	---	---
GMA	---	---	5.6	---
BA	---	---	---	80
Other Ingredients (% of total mix)				
Aromatic 100	---	8	8	12.8
DTBP	0.5	2	2	0.2
Reaction Conditions				
Reaction Temp (°C)	273	232	240	199
Residence Time (min)	12	12	12	12
Flow Modifier Characteristics				
Mn ^a	1,400	1,390	1,480	4,000
Mw ^a	2,900	2,670	2,870	15,200
PDI = Mw/Mn	2.07	1.92	1.94	3.80
Tg ^b	56	47	54	-35
RED # ^c	0.91	0.86	0.88	0.79
Refractive Index ^d	1.592	1.571	1.588	1.491

*a) Gel permeation chromatography (GPC) on PS standards**b) Differential Scanning Calorimetry (DSC) @ 10°C/min (mid point)**c) Relative Energy Difference of FM against polycarbonate computed as reported in Hansen Solubility Parameters – A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 - 13.**d) Refractive Index (R.I.) of polycarbonate = 1.586. Note that FM A to D have different R.I.s.*

[0079] *Example 1 . Enhanced Flow Formulations for Transparent Polycarbonate Injection Molding Applications*

[0080] *To obtain enhanced flow formulations 97 parts of polycarbonate (Lexan 141 G.E. Plastics (GEP) were formulated,*

dry-blended and compounded using a temperature profile from 260°C to 290°C with 3 parts of flow modifiers A, B and C of this invention. Said formulations were injection molded into ASTM test specimens maintaining the barrel and nozzle temperature of the injection molder extruder between 275°C and 280°C, an injection pressure of 9.31 MPa, and the mold temperature was controlled at 88°C. Resulting products showed outstanding balance of moldability, impact strength, HDT, mechanical properties and transparency in comparison to the unmodified plastic. The fact that high transparency is achieved in the final molded products in spite of the refractive index (R.I.) mismatch between the polycarbonate and the FMs of this invention demonstrates the high miscibility of these FMs, given by the low RED number, in polycarbonate. These compounds are useful in injection molding applications involving high shear (thin wall or large pieces) where transparency is a requirement, such as mobile phone housings and housings for other electronic devices. Comparative results are shown below in Table 2.

Table 2. Evaluation of Flow Modifiers in Transparent Polycarbonate Formulations

	Method	Units	Lexan – 141 Control	+FM A	+FM B	+FM C
Modifier Level (wt. % in compound)			0	3	3	3
MFI (@ 300°C/1.2 kg)	ASTM D1238	(g/10 min)	11.6	15.5	14.3	15.0
MFI Increase (% vs. control)	ASTM D1238	%	---	33.6	23.3	29.3
HDT (@ 1.8 MPa)	ASTM D648	°C	130.5	126.2	126.0	124.5
Notched Izod Impact (3.2 mm)*	ASTM D256	J/m	934	763	779	801
Tensile Strength (@ yield)	ASTM D638	MPa	62.1	64.5	65.4	65.7
Elongation @ Yield	ASTM D638	%	7.0	6.9	7.2	6.6
Elongation @ Break	ASTM D638	%	195	161	194	181
Flexural Strength	ASTM D790	MPa	91.0	87.6	88.3	90.3
Flexural Modulus	ASTM D790	MPa	2,200	2,130	2,110	2,130
Young's Modulus	ASTM D638	MPa	1,485	1,565	1,430	1,660
Haze (unpolished samples) (unaged)	ASTM D1003	%	7.4	7.3	6.9	7.3
Haze (unpolished samples) (aged 500 hours @ 120°C)	ASTM D1003	%	8.8	8.8	5.2	6.6

[0081] *Example 2 . Enhanced Flow and Impact Formulations for Opaque Polycarbonate Injection Molding Applications of Thin Wall Pieces.*

[0082] *In order to produce enhanced flow polycarbonate formulations showing outstanding flow and impact resistance in*

thin wall moldings, 88 100 parts of polycarbonate (Lexan EXL 1414 from GEP) were dry-blended with 3 parts of flow modifier D of this invention, 5 parts of methyl methacrylate–butadiene–styrene (MBS) acrylic impact modifier (Rohm & Haas Company, Philadelphia, PA), and 4 parts of TiO_2 . Said formulation was compounded using a temperature profile from 250°C to 270°C. The compound and the unmodified control were then injection molded into a 5x5x1 mm radial flow mold at the abusively high shear rates provided by a 90% injection speed, 8.2 MPa injection pressure and a temperature profile from 280°C to 305°C. The moldings showed outstanding moldability and impact resistance without signs of delamination or additive juicing. These compounds are useful in injection molding applications involving high shear (thin wall or large pieces) where high impact and high crack resistance are needed, such as housings for electronic devices. Comparative results are shown below in Table 3.

Table 3. Evaluation of Flow Modifiers in Thin Wall Polycarbonate Formulations

Modifier Level (% in compound)	Method	Units	Control	Formula Example 2
			0	3
Drop-Weight Impact Strength (on 5 samples at given weight)	ASTM D302	@ 8 lbf	All failed ^a	All passed ^b
Drop-Weight Impact Strength (on 5 samples at given weight)	ASTM D302	@ 25 lbf	All failed ^a	All passed ^b

a) fail = thin walled test specimen cracks

b) pass = thin wall test specimen dents without cracking

[0083] *II. High Flow PC/ABS Blend Compositions*

[0084] Preparation of Flow Modifiers II: In order to provide high flow PC/ABS formulations for injection molding applica-

tions, four different styrene-acrylic flow modifiers, labeled FM E to H below, were designed and prepared in a 2 gallon free radical continuous polymerization reactor system according to the teachings of *US Patent 6,605,681*. The specific synthesis conditions and characterization parameters are given in Table 4 below. The abbreviations used below are defined as follows, STY = styrene, BMA = butyl methacrylate, BA = butyl acrylate, AMS = alpha-methyl styrene, AA = acrylic acid, MAH = maleic anhydride, DTBP = di-tertiary butyl peroxide, A-100 = Aromatic 100 solvent (Exxon), MAK = methyl amyl ketone.

Table 4. Flow Modifier Preparation II.

	Flow Modifier E	Flow Modifier F	Flow Modifier G	Flow Modifier H
Monomer Feed Composition (% of monomer feed)				
STY	71.3	79.3	79.6	80.0
BMA	---	10.6	15.9	---
BA	9.3	---	4.5	---
AMS	18.4	---	---	14.0
AA	1.0	10.1	---	---
MAH	---	---	---	6.0
Other Ingredients (% of total mix)				
Aromatic 100	---	1.00	10.0	---
MAK	---	---	---	6.0
Acetone	---	---	---	4.0
DTBP	2.35	2.15	1.0	2.3
Reaction Conditions				
Reaction Temp (°C)	226	246	208	257
Residence Time (min)	12	12	12	12
Flow Modifier Characteristics				
Mn ^a	1,860	1,200	3,800	1,200
Mw ^a	3,900	2,200	11,100	2,200
PDI = Mw/Mn	2.10	1.83	2.92	1.83
Tg ^b	54	50	59	57
RED # ^c	0.86	0.76	0.85	0.81

a) GPC on PS standards

b) DSC @ 10 °C/min (mid point)

c) Relative Energy Difference of FM against PC/ABS computed as reported in Hansen Solubility Parameters – A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 - 13.

[0085] *Example 3. Enhanced Flow Formulations for PC/ABS (low ABS) Injection Molding Applications with Outstanding Balance of Flow, Vicat Softening Temperature (VST) and Impact Resistance*

[0086] To obtain enhanced flow formulations 95 to 97 parts of a

low ABS content PC/ABS blend (Cyclooy 1200 from GEP) were dry-blended and compounded using a temperature profile from 260°C to 275°C with 3 to 5 parts of flow modifiers E, F and G of this invention. Said formulations were injection molded into ASTM test specimens using a temperature profile from zone 1 to nozzle between 275°C and 280°C at an injection pressure of 5.17 MPa. Mold temperature was controlled at 88°C. The melt viscosity of said formulations were determined by capillary rheometry, using the method described in ASTM D3835-96. A Goettfert Rheograph 2003 Capillary Rheometer was used, having a 12mm barrel diameter, a 0.5mm inner diameter, a die length of 20mm, and a 180° die entry angle. The measurements were performed at 300°C, using a six minute preheating time. The resulting products showed outstanding balance of moldability, impact strength, and VST, in comparison to the unmodified plastic. These compounds are useful in injection molding applications involving high shear (thin wall or large pieces) where outstanding impact resistance and VST are requirements. Such applications include housings for mobile phones and other electronic devices. Comparative results are shown below in Table 5.

Table 5. Evaluation of Flow Modifiers in PC/ABS (low ABS) Formulations

	Method	Units	C-1200 Control Injected	C-1200 Control Extruded	C-1200 +FM E	C-1200 +FM E	C-1200 +FM F	C-1200 +FM F	C-1200 +FM G	C-1200 +FM G
Modifier Level (% in compound)			0	0	3	5	3	5	3	5
MF1 (230°C/3.8 kg)	ASTM D1238	(g/10 min)	2.1	2.3	2.7	3.3	3.4	4.7	2.7	3.4
MF1 Increase (% vs. control)	ASTM D1238	%	---	9.5	28.6	57.1	61.9	123.8	28.6	61.9
VST (@ 50 N)	ASTM D648	°C	134.0	133.8	131.7	128.4	128.7	126.1	131.4	129.1
Notched Izod Impact (3.2 mm)	ASTM D256	J/m	737	731	785	849	694	774	758	667
Capillary Rheometry Viscosity	ASTM D3835	cps								
1,000s-1			--	102,000	--	64,100	--	40,500	--	49,500
10,000s-1			--	30,200	--	23,300	--	21,800	--	28,500

[0087] *Example 4. Enhanced Flow Formulations for PC/ABS (high ABS) Injection Molding Applications with Outstanding Balance of Flow, VST and Impact Resistance*

[0088] To obtain enhanced flow formulations 95 to 97 parts of a

high ABS content PC/ABS blend (Cyclooy 1000HF from GEP) were dry-blended with 3 to 5 parts of flow modifiers E, F and G of this invention and compounded and injection molded at conditions given in Example 3. Resulting products showed an outstanding balance of moldability, impact strength, and VST, in comparison to the unmodified plastic. These compounds are useful in injection molding applications involving high shear (thin wall or large pieces) where outstanding impact resistance and VST are requirements, such as housings for mobile phones and other electronic devices. Comparative results are shown below in Table 6.

Table 6 Evaluation of Flow Modifiers in PC/ABS (high ABS) Formulations

	Method	Units	C-1000 Control Injected	C-1000 Control Extruded	C-1000 +FM E	C-1000 +FM E	C-1000 +FM F	C-1000 +FM F	C-1000 +FM G	C-1000 +FM G
Modifier Level (% in compound)			0	0	3	5	3	5	3	5
MFI (230°C/3.8 kg)	ASTM D1238	(g/10 min)	6.0	6.0	7.1	8.0	8.0	10.3	7.5	8.3
MFI Increase (% vs. control)	ASTM D1238	%	----	0.0	18.3	33.3	33.3	71.7	25.0	38.3
VST (@ 50 N)	ASTM D648	°C	113.0	114.8	112.7	111.3	112.4	110.5	112.3	111.2
Notched Izod Impact (3.2 mm)	ASTM D256	J/m	571	518	480	518	443	363	1,078	491

[0089] *Example 5. Enhanced Flow Formulations for PC/ABS (low ABS) Fire Retardant Injection Molding Applications.*

[0090] In order to produce a fire retardant (FR) PC/ABS formulation showing outstanding flow, impact resistance and fire

retardancy 97.1 and 95.2 parts of FR PC/ABS (Bayblend FR 2010; Bayer Polymers) were formulated, dry-blended and compounded in a Brabender 15mm Conical Twin Screw Co-Rotating Extruder, using a temperature profile between 230°C and 250°C with 2.9 and 4.8 parts of flow modifiers E and F of this invention. Said formulations were injection molded using a Battenfeld 29M ton injection Molding Machine into ASTM test specimens maintaining the barrel and nozzle temperature of the injection molder extruder between 240°C and 265°C, an injection pressure of 14.0 MPa, and the mold temperature was controlled at 54°C.

[0091] The molded parts showed an outstanding balance of moldability, impact strength, VST, and mechanical properties in comparison to the unmodified plastic without signs of delamination or juicing. These compounds are useful in injection molding applications requiring high shear (thin wall or large pieces) and fire retardancy, such as housings for electronic devices, personal care items, and household appliances. Comparative results are shown below in Table 7.

Table 7. Evaluation of Flow Modifiers in FR PC/ABS (low ABS) Formulations

	Modifier Level (% in compound)	Melt Index (MFI)	Notched Izod Impact	Vicat Softening Point (VST)	Tensile Stress @ Yield
Test Method		ASTM D1238 (260°C/5kg)	ASTM D256 (3.2 mm)	ASTM D1525 (Rate B: 5kg; 120°C/h)	ASTM D639
Units		(g/10min)	(J/m)	(°C)	(MPa)
FR-2010 Control Injected	0	32.0	528	107.8	55.0
FR-2010+E	2.9	34.0	467	105.0	55.0
FR-2010+E	4.8	40.0	431	104.4	54.9
FR-2010+F	2.9	36.0	447	105.6	55.5
FR-2010+F	4.8	36.0	411	104.4	55.4

[0092] *Example 6. Enhanced Flow Formulations for PC/ABS (high ABS) Fire Retardant Injection Molding Applications.*

[0093] In order to produce a FR PC/ABS formulation showing outstanding flow, impact resistance and fire retardancy

between 97.1 and 95.2 parts of FR PC/ABS (Bayblend FR 2000; Bayer Polymers) were formulated, dry blended, and compounded using the conditions stated in Example 5 with between 2.9 and 4.8 parts of flow modifiers F and H of this invention. Said formulations were injection molded using the conditions stated in Example 5.

[0094] The molded parts showed an outstanding balance of moldability, impact strength, VST, and mechanical properties in comparison to the unmodified plastic without signs of delamination or juicing. These compounds are useful in injection molding applications requiring high shear (thin wall or large pieces) and fire retardancy, such as housings for electronic devices, personal care items, and household appliances. Comparative results are shown below in Table 8.

Table 8. Evaluation of Flow Modifiers in FR PC/ABS (high ABS) Formulations

	Modifier Level (% in compound)	Melt Index (MFI)	Notched Izod Impact	Vicat Softening Point (VST)	Tensile Stress @ Yield
Test Method		ASTM D1238 (260°C/5kg)	ASTM D256 (3.2 mm)	ASTM D1525 (Rate B: 5kg; 120°C/h)	ASTM D639
Units		(g/10min)	(J/m)	(°C)	(MPa)
FR-2000 Control Injected	0	26.0	499	91.7	54.3
FR-2000+H	2.9	32.0	472	90.6	54.7
FR-2000+H	4.8	34.0	352	90.0	53.1
FR-2000+F	2.9	32.0	472	90.0	54.7
FR-2000+F	4.8	37.0	382	88.9	54.3

[0095] *III. High Flow Polyesters and Polyester/Thermoplastics Blend Compositions*

[0096] Preparation of Flow Modifiers III:

[0097] In order to provide high flow polyester formulations for injection molding applications, flow modifiers C and F of this invention were evaluated along with two different styrene-acrylic flow modifiers, labeled FM J and K below, which were designed, and then prepared in a 2 gallon free radical continuous polymerization reactor system according to the teachings of *US Patent 6,605,681*. The specific synthesis conditions and characterization parameters are given in Table 9 below. The abbreviations used below are defined as follows, STY = styrene, MMA = methyl methacrylate, BA = butyl acrylate, IPA = iso-propyl alcohol, DTAP = di-tertiary amyl peroxide, DTBP = di-tertiary butyl peroxide, A-100 = Aromatic 100 solvent (Exxon).

Table 9. Flow Modifier Preparation III

	Flow Modifier -J	Flow Modifier K
Monomer Feed Composition (% of monomer feed)		
STY	---	50.7
MMA	---	49.3
BA	100	---
Other Ingredients (% of total mix)		
IPA	4.2	---
A-100	---	0.9
DTAP	1.5	---
DTBP	---	2.2
Reaction Conditions		
Reaction Temp (°C)	243	206
Residence Time (min)	12	12
Flow Modifier Characteristics		
Mn ^a	1,100	1,700
Mw ^a	1,700	4,000
PDI = Mw/Mn	1.54	2.35
Tg ^b	-66	52
RED # ^c	1.22	1.35

a) GPC on PS standards

b) DSC @ 10°C/min (mid point)

c) Relative Energy Difference of FM against PBT computed as reported in Hansen Solubility Parameters – A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 - 13.

[0098] *Example 7. Enhanced Flow Formulations for Polyester Injection*

Molding Applications To obtain enhanced flow formulations 95 to 97 parts of poly(butylene terephthalate) (PBT) (Valox 325 from GEP) were dry-blended with 3 to 5 parts of flow

modifiers C, F, J and K of this invention and compounded using a temperature profile from 230°C to 250°C. Said formulations were injection molded into ASTM test specimens using a temperature profile from zone 1 to nozzle between 270°C and 280°C at an injection pressure of 4.14 MPa, mold temperature was controlled at 65°C. The resulting products show outstanding balance of moldability, impact strength, VST, and mechanical properties in comparison to the unmodified plastic. These compounds are useful in injection molding applications involving high shear (thin wall or large pieces) where an excellent balance of moldability, impact resistance, VST and mechanical properties is a requirement, such as in automobile parts, including indicator panels and mirror housings and housings for appliances and some electronic devices.

Comparative results are shown below in Table 10.

Table 10. Evaluation of Flow Modifiers in PBT Formulations

	Method	Units	V-325 Control Extruded	+FM J	+FM K	+FM L	+FM M	+FM F
Modifier Level (% in compound)			0	5	5	5	3	5
MFI (230°C/2.16 kg)	ASTM D1238	(g/10 min)	6.5	7.5	12.9	7.5	10.8	11.6
MFI Increase (% vs. control)	ASTM D1238	%	---	15.4	98.5	15.4	66.2	78.5
VST (@ 50 N)	ASTM D648	°C	170.3	167.8	162.7	172.1	174.2	170.6
Notched Izod Impact (3.2 mm)	ASTM D256	J/m	32	43	27	27	32	27
Tensile Strength (@ yield)	ASTM D638	MPa	56.8	52.0	53.5	57.5	57.9	57.9
Elongation @ Yield	ASTM D638	%	3.4	4.3	3.7	3.8	3.9	3.7
Elongation @ Break	ASTM D638	%	10.7	19.5	9.1	8.4	11.1	10.6
Young's Modulus	ASTM D638	MPa	2,524	2,441	2,662	2,931	2,745	2,786

[0099] *Example 8 . Enhanced Flow Formulations for Glass Fiber Reinforced Polyester Injection Molding Applications*

[0100] *To obtain enhanced flow formulations 95 to 97 parts of glass fiber reinforced poly(butylene terephthalate) (Valox*

420 from GEP) were dry-blended with 3 to 5 parts of flow modifiers C, F, J and K of this invention and compounded and molded under the same conditions as Example 7. Resulting products showed outstanding balance of moldability, impact strength, VST, and mechanical properties in comparison to the unmodified plastic. These compounds are useful in injection molding applications involving high shear and complicated molds (large pieces) where an extremely high VST and an excellent balance of moldability, impact resistance, and mechanical properties are requirements, such as automobile parts, including indicator panels, mirror, and headlamps housings. Comparative results are shown below in Table 11.

Table 11. Evaluation of Flow Modifiers in Glass Fiber Reinforced PBT Formulations

Modifier Level (% in compound)	Method	Units	V-420 Control Extruded	+FM J	+FM K	+FM C	+FM F	+FM P
MFI (230°C/2.16 kg)	ASTM D1238	(g/10 min)	0	5	5	5	3	5
MFI Increase (% vs. control)	ASTM D1238	%	7.2	10.2	12.8	9.3	12.9	17.5
VST (@ 50 N)	ASTM D648	°C	207.3	202.7	203.9	203.9	205.7	200.3
Notched Izod Impact (3.2 mm)	ASTM D256	J/m	43	112	43	53	43	37
Tensile Strength (@ yield)	ASTM D638	MPa	99.3	82.8	93.1	95.9	95.9	89.7
Elongation @ Yield	ASTM D638	%	3.0	3.3	2.8	2.9	2.9	2.4
Elongation @ Break	ASTM D638	%	3.1	3.6	3.0	3.2	2.9	2.4
Young's Modulus	ASTM D638	MPa	8,069	6,966	7,034	7,586	7,724	7,586

[0101] *IV. High Flow Polyamide Compositions Preparation of Flow Modifiers IV:*

[0102] In order to provide high flow polyamide and polyamide-based blend formulations for injection molding applica-

tions, flow modifier K of this invention was evaluated along with three other styrene-acrylic flow modifiers, labeled FM L, M, and N below, which were designed, and then prepared in a 2 gallon free radical continuous polymerization reactor system according to the teachings of U.S. Patent Application 09/354,350. The specific synthesis conditions and characterization parameters are given in Table 12 below. The abbreviations used below are defined as follows, STY = styrene, AA = acrylic acid, BA = butyl acrylate, 2-EHA = 2-ethylhexyl acrylate, EA = ethyl acrylate, IPA = iso-propyl alcohol, DTBP = di-tertiary butyl peroxide, A-100 = Aromatic 100 solvent (Exxon).

Table 12. Flow Modifier Preparation IV.

	Flow Modifier L	Flow Modifier M	Flow Modifier N
Monomer Feed Composition (% of monomer feed)			
STY	91.47	--	--
AA	5.43	--	--
BA	--	25	10
2-EHA	--	75	--
EA	--	--	90
Other Ingredients (% of total mix)			
IPA	--	5	5
Xyene	--	4	4
A-100	0.9	--	--
DTBP	2.2	1	1
Reaction Conditions			
Reaction Temp (°C)	243	230	225
Residence Time (min)	12	12	12
Flow Modifier Characteristics			
Mn ^a	1,500	1,400	1,400
Mw ^a	2,900	2,600	3,000
PDI = Mw/Mn	1.93	1.91	2.11
Tg ^b	66	-69	-34
RED # ^c	2.16	1.86	1.64

a) GPC on PS standards

b) DSC @ 10 °C/min (mid point)

c) Relative Energy Difference of FM against PA 6 computed as reported in Hansen Solubility Parameters – A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 - 13.

[0103] *Example 9. Enhanced Flow Formulations for Polyamide Injection Molding Applications.* To obtain enhanced flow formulations 95 and 97 parts of polyamide 6 (Ultramide B3, Bayer Polymers) were melt blended with 3 and 5 parts flow modifier

N of this invention using a Brabender Plasticorder Mixing Bowl. The melt was blended for 2 to 5 minutes, maintaining the temperature profile between 250°C and 280°C. The resulting compounds demonstrate outstanding flow properties when compared to the unmodified polyamide 6. Comparative results are shown below in Table 13.

[0104]

Table 13. Evaluation of Flow Modifiers in Polyamide 6,6.

	Units	PA 6 Control	+FM N	+ FM N
Modifier Level (% in compound)		0	3	5
MFI (270°C/1.2 kg)	(g/10 min)	42.8	47.6	50.3
MFI Increase (% vs. control)	%	---	11	17

[0105] *Example 10. Enhanced Flow Formulations for Polyamide Injection Molding Applications.*

[0106] To obtain enhanced flow formulations 95 and 97 parts of polyamide 6,6 (Zytel L101, DuPont) were melt blended

with 3 and 5 parts flow modifiers M and N of this invention using a Brabender Plasticorder Mixing Bowl. The melt was blended for 2 to 5 minutes, maintaining the temperature profile between 250°C and 280°C. The resulting compounds demonstrate outstanding flow properties when compared to the unmodified polyamide 6,6. Comparative results are shown below in Table 14.

Table 14. Evaluation of Flow Modifiers in Polyamide 6.

	Units	PA 6,6 Control	+FM M	+FM N	+ FM N
Modifier Level (%) in compound)		0	5	3	5
MFI (270°C/1.2 kg)	(g/10 min)	34.0	41.8	38.4	38.1
MFI Increase (% vs. control)	%	---	23	13	12

[0107] *Example 11. Enhanced Flow Formulations for Reinforced Polyamide Injection Molding Applications*

[0108] To obtain enhanced flow formulations 82 parts of polyamide 6,6 (PA 6,6) (Rhodia) were dry-blended with 3

parts of flow modifiers K and L of this invention and compounded using a temperature profile from 270°C to 290°C with lateral feed of 15 parts of glass fiber (GF). Said formulations were injection molded into ASTM test specimens using a temperature profile from zone 1 to nozzle between 280°C and 300°C. Resulting products show outstanding balance of moldability, impact strength, and mechanical properties in comparison to the unmodified plastic. These compounds are useful in injection molding applications involving complicated molds and high shear (large pieces) where an excellent balance of moldability, impact resistance, and mechanical properties is a requirement, such as under-the-hood automobile parts, including engine covers and other parts. Comparative results are shown below in Table 15.

Table 15. Evaluation of Flow Modifiers in Polyamide Formulations

	Method	Units	PA 6,6 + 15% GF Control	+FM K	+FM L
Modifier Level (%) in compound)			0	3	3
MFI (300°C/1.2 kg)	ASTM D1238	(g/10 min)	25.8	34.5	29.3
MFI Increase (% vs. control)	ASTM D1238	%	---	33.7	13.6
Notched Izod Impact (3.2 mm)	ASTM D256	J/m	336	315	315
Flexural Modulus (@ yield)	ASTM D790	MPa	3,920	3,770	3,820
Elongation @ Break	ASTM D638	%	2.2	2.4	2.5

[0109] *V. High Flow Poly(Phenylene Ether) Blend Compositions*

[0110] In order to provide increased flow poly(phenylene Ether) based blend formulations for injection molding applica-

tions, flow modifiers A and H of this invention was evaluated along with another styrene-acrylic flow modifier, labeled FM O below, which was designed, and then prepared in a 2 gallon free radical continuous polymerization reactor system according to the teachings of U.S. Patent 6,605,681. The specific synthesis conditions and characterization parameters are given in Table 16 below. The abbreviations used below are defined as follows, STY = styrene, AMS = alpha methyl styrene, MAH = maleic anhydride, DTBP = di-tertiary butyl peroxide.

Table 16. Flow Modifier Preparation V.

	Flow Modifier O
Monomer Feed Composition (% of monomer feed)	
STY	80
AMS	5
MAH	15
Other Ingredients (% of total mix)	
Acetone	10
DTBP	1.9
Reaction Conditions	
Reaction Temp (°C)	240
Residence Time (min)	15
Flow Modifier Characteristics	
Mn ^a	1,600
Mw ^a	3,400
PDI = Mw/Mn	2.15
Tg ^b	87
RED # ^c	0.57

a) GPC on PS standards

b) DSC @ 10 °C/min (mid point)

c) Relative Energy Difference of FM against PPO
computed as reported in *Hansen Solubility
Parameters – A Users Handbook*, C. M. Hansen,
CRC Press, 2000, pp. 1 - 13.

[0111] *Example 12 Enhanced Flow Formulations for Poly(phenylene ether)*

Based Blends for Injection Molding Applications

[0112] To obtain enhanced flow formulations 98 and 96 parts of a PPE, styrenic blend (Noryl N190, GEP) were formulated,

dry-blended and compounded in a Brabender 15mm Conical Twin Screw Co-Rotating Extruder using a temperature profile between 240°C and 280°C with 2 and 4 parts flow modifiers A, H and O of this invention. Said compositions were injection molded using a Meiki 50 ton injection molding machine into ASTM test specimens maintaining the barrel and nozzle temperature of the injection molder between 230°C and 250°C, an injection pressure of 0.82 MPa, and the mold temperature was controlled at 40°C. The resultant compounds demonstrated an outstanding balance of MFI, moldability, impact strength, VST, and mechanical properties in comparison to the unmodified PPE blends with out the occurrence of juicing or delamination. These compounds are useful in injection molding applications where increased flow is required such as computer equipment and other electronic devices. Comparative results are shown below in Table 17.

Table 17. Evaluation of Flow Modifiers in Poly(Phenylene Ether) Blend Formulations.

Modifier	Level (% in compound)	MFI	Tensile Stress Break	Flexural Stress Break	Izod Impact	Vicat Softening Point
Method	--	ASTM D1238 (280°C/5kg)	ASTM D638 (50mm/min)	ASTM D790 (1.3mm/min)	ASTM D256	ASTM D1525 (Rate B: 5kg; 120°C/h)
Units	--	(g/10min)	(MPa)	(MPa)	(J/m)	°C
Extruded Control	0	35.1	48.4	80.5	208.6	116
+FM A	2	33.0	46.2	80.1	197.6	115
+FM A	4	39.5	46.4	78.2	183.8	124
+FM H	4	39.4	46.5	80.7	189.5	125
+FM O	4	38.6	46.9	79.7	188.8	115

[0113] *V. High Flow Transparent-ABS Compositions Preparation of Flow Modifiers VI:*

[0114] In order to provide high flow in transparent-ABS formulations for injection molding applications, four different

styrene-acrylic flow modifiers, labeled FM J, P, Q, and R below, were designed and prepared in a 2 gallon free radical continuous polymerization reactor system according to the teachings of *US Patent 6,605,681*. The specific synthesis conditions and characterization parameters are given in table 15 below. The abbreviations used below are defined as follows, STY = styrene, MMA = methyl methacrylate, 2-EHA = 2-ethylhexyl acrylate, BA = butyl acrylate, DTAP = di-tertiary amyl peroxide, DTBP = di-tertiary butyl peroxide, IPA = iso-propyl alcohol, A-100 = Aromatic 100 solvent (Exxon).

Table 18. Flow Modifier Preparation VI

	Flow Modifier J	Flow Modifier P	Flow Modifier Q	Flow Modifier R
Monomer Feed Composition (% of monomer feed)				
STY	---	20	---	30
2-EHA	---	---	100	---
MMA	---	---	---	70
BA	100	80	---	---
Other Ingredients (% of total mix)				
IPA	4.2	20	20	---
Aromatic 100	---	---	---	8
DTAP	1.5	---	---	---
DTBP	---	1	1	2
Reaction Conditions				
Reaction Temp (°C)	243	275	275	196
Residence Time (min)	12	12	12	12
Flow Modifier Characteristics				
M _n ^a	1,100	1,200	1,190	1,700
M _w ^a	1,700	2,050	2,020	3,800
PDI = M _w /M _n	1.55	1.71	1.70	2.24
T _g ^b	-66	-45	-65	51
RED # ^c	0.55	0.58	0.65	0.60
Refractive Index ^d	1.4650	1.4899	1.4650	1.5201

*a) GPC on PS standards**b) DSC @ 10 °C/min (mid point)**c) Relative Energy Difference of FM against ABS computed as reported in Hansen Solubility Parameters – A Users Handbook, C. M. Hansen, CRC Press, 2000, pp. 1 - 13.**d) R.I. of Transparent ABS = 1.515 – 1.520. Note that FMs above have different R.I.s.*

[0115] *Example 13. Enhanced Flow Formulations for Transparent-ABS Injection Molding Applications*

[0116] To obtain enhanced flow formulations 100 parts of transparent-ABS (Starex CT- 0520 from Cheil Chemicals) were

formulated, dry-blended with 3 to 9 parts of flow modifiers J, P, Q, and R of this invention and then compounded in a 30 mm twin screw extruder using a temperature profile from 180°C to 200°C. Said formulations were injection molded into ASTM test specimens using a DM Mekei Co, M-50A injection molding machine (50 metric tons of clamping force) fitted with a 28 mm screw. The temperature profile used from zone 1 to nozzle was controlled between 200°C and 190°C. The resulting compounds showed outstanding MFI increases. The resulting molding products showed outstanding balance of moldability, impact strength, HDT, mechanical properties and transparency in comparison to the unmodified plastic. The fact that high transparency is achieved in the final molded products in spite of the R.I. mismatch between transparent-ABS and the FMs of this invention demonstrates the high miscibility of these FMs, given by the low RED number, in this plastic. These compounds are useful in injection molding applications involving high shear (thin wall or large pieces) where transparency is a requirement, such as housings for electronic devices. Comparative results are shown below in Tables 19 and 20.

Table 19. Evaluation of Flow Modifiers in Transparent ABS Formulations*

Formula 100 parts of Transparent ABS (Starex CT-0520) +	MFI (220°C/10 kg (g/10')	HAZE (%)	HAZE Increase (% vs- injected control)	Color (ΔE)	Notched Charpy Impact (Kgf-cm/cm)
Injection Molded Control	15.9	3.0	0.0	0.0	17.2
Extruded/Injected Control	18.6	3.6	0.6	1.5	16.9
FM-J @ 3 phr	28.6	3.3	0.3	0.9	14.6
FM-J @ 5 phr	37.3	4.0	1.0	0.8	13.6
FM-J @ 7 phr	46.1	3.5	0.5	1.8	12.0
FM-P @ 3 phr	29.3	2.4	-0.6	1.2	15.5
FM-P @ 5 phr	34.6	3.3	0.3	3.7	13.2
FM-P @ 7 phr	41.7	4.0	1.0	5.6	14.0
FM-Q @ 3 phr	30.2	3.0	0.0	2.3	15.6
FM-Q @ 5 phr	38.5	2.9	-0.1	4.1	14.5
FM-Q @ 7 phr	47.5	3.6	0.6	2.0	13.6
FM-R @ 5 phr	29.6	3.8	0.8	1.0	13.7
FM-R @ 7 phr	36.8	2.5	-0.5	1.9	10.8
FM-R @ 9 phr	43.1	3.6	0.6	1.4	7.6

* same ASTM methods used in these evaluations as in previous examples.

Table 20. Evaluation of Flow Modifiers in Transparent ABS Formulations*

Formula 100 parts of Transparent ABS (Starex CT-0520) +	TENSILE STRENGTH (Kgf/cm ²)	ELONGATION @ BREAK (5 mm/min) (%)	FLEXURAL STRENGTH (Kgf/cm ²)	FLEXURAL MODULUS (Kgf/cm ²)	VST (°C)	HDT (°C)
Injection molded Control	380	15.2	564	17,624	96.4	77.0
Extruded/Injected Control	390	16.4	586	18,709	97.5	77.5
FM-J @ 3 phr	370	17.2	545	17,442	91.6	72.2
FM-J @ 5 phr	360	13.9	535	17,775	88.7	66.9
FM-J @ 7 phr	340	18.2	505	17,185	84.5	66.0
FM-P @ 3 phr	380	16.9	553	17,767	91.9	71.7
FM-P @ 5 phr	370	14.0	558	17,958	89.3	69.9
FM-P @ 7 phr	360	17.5	532	17,205	87.5	67.8
FM-Q @ 3 phr	370	9.5	537	17,735	93.2	71.3
FM-Q @ 5 phr	350	13.4	510	16,845	88.0	66.9
FM-Q @ 7 phr	340	12.9	491	16,487	86.5	66.6
FM-R @ 5 phr	390	15.3	562	18,055	95.6	75.2
FM-R @ 7 phr	400	12.7	571	18,225	93.7	74.1

* same ASTM methods used in these evaluations as in previous examples.

[0117] *Example 14 . Enhanced Flow Formulations for High Temperature*

Polycarbonate Applications.

[0118] *In order to produce enhanced flow polycarbonate formulations showing outstanding resistance to thermal degra-*

dation in thin wall moldings, 98 parts of a polycarbonate were dry-blended with 2 parts of flow modifier F of this invention. Said formulation was compounded using procedures recommended in the literature and pelletized. The thermal stability of said compound was determined using a TA Instruments AutoTGA 2950 instrument operated isothermally at 270°C and 300°C and dynamically using a 5°C / minute heating ramp from room temperature to 500°C. The compound demonstrated outstanding thermal stability. This compound would be useful in injection molding applications involving high shear (thin wall or large pieces) where high thermal resistance is needed, such as housings for electronic devices. Comparative results are shown in Table 21.

Table 21. Evaluation of Flow Modifier F in Polycarbonate Formulations

Test Methodology				
Isothermal	Units	10 minutes	20 minutes	30 minutes
Weight Loss at 270°C	%	0.03	0.07	0.10
Weight Loss at 270°C	%	0.30	0.46	0.57
Dynamic		270°C	300°C	320°C
Weight Loss	%	0.06	0.16	0.32

[0119] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of sub-

ranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like include the number recited and refer to ranges which can be subsequently broken down into sub-ranges as discussed above.

- [0120] While preferred embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with one of ordinary skill in the art without departing from the invention in its broader aspects. Various features of the invention are defined in the following claims.